National Institute of Standards & Technology

# Certificate of Analysis

## Standard Reference Material® 695

### Trace Elements in Multi-Nutrient Fertilizer

This Standard Reference Material (SRM) is intended primarily for use in the evaluation of techniques employed in the analysis of multi-nutrient fertilizer materials and materials of a similar matrix. One unit of SRM 695 consists of approximately 70 g of jet-milled fertilizer.

**Certified Values:** The certified concentrations for 17 elements, expressed as mass fractions [1] on a dry basis, are provided in Table 1. Certified values are based on results from critically evaluated independent analytical techniques. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST [2].

**Reference Values:** The reference values for 5 constituents, expressed as mass fractions on a dry basis, are provided in Table 2. The reference values are based on results obtained from a single NIST analytical method. Reference values are non-certified values that are the best estimate of the true value; however, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may not include all sources of uncertainty [2].

**Information Values:** The values for two elements are provided in Table 3 for information purposes only. These are non-certified values with no uncertainty assessed. The information values included in this certificate are based on results from one NIST method.

**Expiration of Certification:** The certification of SRM 695 is valid, within the measurement uncertainties specified, until **01 April 2016**, provided the SRM is handled in accordance with the instructions given in this certificate (see "Instructions for Use"). This certification is nullified if the SRM is contaminated or otherwise modified.

**Maintenance of SRM Certification:** NIST will monitor representative samples of this SRM over the period of its certification. If substantive changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

E.A. Mackey of the NIST Analytical Chemistry Division was responsible for coordination of the technical measurements leading to certification.

Statistical analyses leading to the certified and reference values were performed by S.D. Leigh of the NIST Statistical Engineering Division.

The support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

Stephen A. Wise, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 26 June 2006

Robert L. Watters, Jr., Chief
Measurement Services Division

## INSTRUCTIONS FOR USE

**Sampling:** The SRM should be thoroughly mixed by repeatedly inverting and rotating the bottle horizontally before sampling. A minimum sample mass of 200 mg should be used for analytical determinations to be related to elemental concentration values provided. The SRM should be stored in its original, tightly sealed bottle away from intense sources of heat.

**Drying:** In order to relate measurements to the certified and reference values that are expressed on a dry mass basis, users should determine a drying correction at the time of each analysis. The recommended drying procedure is desiccator drying of portions with a depth ≤ 0.5 cm, for two weeks, over fresh magnesium perchlorate. The average mass loss measured at NIST using this method for six portions of SRM 695 was 1.34 % (1 s = 0.06 %). Oven drying, even at relatively low temperatures (85 °C), can result in decomposition of the carbonate and ammonium (and possibly other) compounds in this blended fertilizer material. **DO NOT** dry SRM 695 in an oven to determine the dry-mass basis.

## SOURCE, PREPARATION, AND ANALYSIS

This multi-nutrient blended fertilizer was developed in collaboration with members of the Association of American Plant Food Control Officials (AAFPCO) and The Fertilizer Institute (TFI). The material used to prepare SRM 695 was provided to NIST by William L. Hall Jr. (The Mosaic Company). The material consists of urea, diammonium hydrogen phosphate, calcium carbonate, potassium chloride, potassium nitrate, and potassium magnesium sulfate, and various other metal sulfates. The material was ground and shipped to NIST where the material was jet-milled, blended, and bottled by C. Fales of the Measurement Services Division.

Analyses of this material used for certification were performed at NIST (Gaithersburg, MD) and at the United States Geological Survey (Denver, CO). The analytical techniques used for each element are listed in Table 4; the analysts are listed in Table 5.

Table 1. Certified Values for Selected Elements (Dry Mass Basis) in SRM 695

Major and Minor Constituent Elements [(a)]

| Elements | Mass Fraction (%) | | Mass Fraction (%) |
|---|---|---|---|
| Calcium | 2.26 ± 0.04 | Manganese | 0.305 ± 0.005 |
| Iron | 3.99 ± 0.08 | Sodium | 0.405 ± 0.007 |
| Magnesium | 1.79 ± 0.05 | Potassium | 11.65 ± 0.13 |
| | | Zinc | 0.325 ± 0.005 |

Trace Elements [(a)]

| Elements | Mass Fraction (mg/kg) | Elements | Mass Fraction (mg/kg) |
|---|---|---|---|
| Arsenic | 200 ± 5 | Mercury | 1.955 ± 0.036 |
| Cadmium | 16.9 ± 0.2 | Molybdenum | 20.0 ± 0.3 |
| Chromium | 244 ± 6 | Nickel | 135 ± 2 |
| Cobalt | 65.3 ± 2.4 | Lead | 273 ± 17 |
| Copper | 1225 ± 9 | Vanadium | 122 ± 3 |

[(a)] Certified values for all elements except arsenic and mercury are the unweighted means of results from two or three analytical methods. The uncertainty listed with each value is an expanded uncertainty about the mean, with coverage factor 2, calculated by combining a between-method variance with a pooled, within method variance [3] following the ISO and NIST Guides [4]. The certified values for As and Hg are each results from a single NIST method (INAA for As, and CV-ID-ICP-MS for Hg) for which a complete evaluation of all sources of

uncertainty has been performed. The uncertainty for each certified value represents an expanded uncertainty with a coverage factor of 2, with uncertainty components combined following the ISO and NIST Guides [4].

Table 2. Reference Values (Dry Mass Basis) for Selected Elements in SRM 695

Major and Minor Constituent Elements [a]

| Element | Mass Fraction (%) |
|---|---|
| Aluminum | 0.61 ± 0.03 |
| Boron | 0.111 ± 0.002 |
| Nitrogen | 13.9 ± 0.4 |
| Phosphorous | 7.2 ± 0.1 |

Trace Elements [a]

| Elements | Mass Fraction (mg/kg) |
|---|---|
| Selenium | 2.1 ± 0.1 |

[a] Reference values for all elements except aluminum are based on results of one analytical method at NIST and the uncertainty values represent the expanded uncertainties which include the combined Type A and Type B with a coverage factor of 2, following the ISO and NIST Guides [4]. The certified value for aluminum is the unweighted mean of results from two analytical methods and the uncertainty listed is an expanded uncertainty about the mean, with coverage factor 2, calculated by combining a between-method variance with a pooled, within method variance [3] following the ISO and NIST Guides [4].

Table 3. Information Values (Dry Mass Basis) for Selected Elements in SRM 695 [a]

| Element | Mass Fraction |
|---|---|
| Chlorine | 4.6 % |
| Titanium | 310 mg/kg |

[a] Information values are based on results of one analytical method at NIST.

Table 4. Methods of Analysis for SRM 695

| Element | Method(s) |
|---|---|
| Al | INAA, XRF |
| As | INAA |
| B | PGAA |
| Ca | XRF, INAA |
| Cd | ID-ICP-MS, PGAA |
| Cl | INAA |
| Co | INAA, XRF |
| Cr | INAA, XRF |
| Cu | ID-ICP-MS, ICP-OES, XRF |
| Fe | INAA, PGAA, XRF |
| Hg | CV ID-ICP-MS |
| K | PGAA, XRF |
| Mg | INAA, XRF |
| Mn | PGAA, XRF, INAA |
| Mo | ICP-OES, XRF |
| N | PGAA |
| Na | INAA, XRF |
| Ni | ICP-OES, XRF |
| P | XRF |
| Pb | ICP-OES, XRF |
| Se | INAA |
| Ti | XRF |
| V | INAA, XRF |
| Zn | INAA, XRF |

**Methods:**

| | |
|---|---|
| CV ID-ICP-MS | Cold Vapor, Isotope Dilution, Inductively Coupled Plasma Mass Spectrometry |
| ICP-OES | Inductively Coupled Plasma Optical Emission Spectrometry |
| ID-ICP-MS | Isotope Dilution Inductively Coupled Plasma Mass Spectrometry |
| INAA | Instrumental Neutron Activation Analysis |
| HG-AAS | Hydride Generation Atomic Absorption Spectrometry |
| PGAA | Prompt Gamma-ray Activation Analysis |
| XRF | X-ray Fluorescence Spectrometry |

Table 5. Analysts for SRM 695

NIST Analytical Chemistry Division

| | |
|---|---|
| S.E. Long | M.S. Rearick |
| E.A. Mackey | J.R. Sieber |
| R. Oflaz | L.J. Wood |
| A.F. Marlow | L.L. Yu |
| K.E. Murphy | |

United States Geological Survey; Denver, CO

| | |
|---|---|
| S.A. Wilson | Z.A. Brown |
| P.H. Briggs | J. Budahn |

## REFERENCES


[1] Taylor, B.N.; *Guide for the Use of the International System of Units (SI)*, NIST Special Publication 811 (1995).

[2] May, W.E.; Gills, T.E.; Parris, R.; Beck, II, C.M.; Fassett, J.D.; Gettings, R.J.; Greenberg, R.R.; Guenther, F.R.; Kramer, G.; MacDonald, B.S.; Wise, S.A.; *Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*, NIST Special Publication 260-136 (1999).

[3] Levenson, M.S.; Banks, D.L.; Eberhardt, K.R.; Gill, L.M.; Guthrie, W.F.; Liu, H.K.; Vangel, M.G.; Yen, J.H.; Zhang, N.F.; J. Res. NIST 105, pp. 571-549 (2000).

[4] ISO; *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st ed.; International Organization for Standardization: Geneva, Switzerland (1993); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*, NIST Technical Note 1297, U.S. Government Printing Office, Washington, DC (1994); available at http://physics.nist.gov/Pubs/.


*Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.*

ADDENDUM

Results from Test Method for Determination of Analysis of As, Cd, Co, Cr, Mo, Ni, Pb, and Se in Fertilizers by Microwave Digestion in Nitric Acid and ICP-OES Detection

The certified, reference and information values presented in the Certificate of Analysis for SRM 695 represent the total element content per unit mass of material. These values are obtained either from methods that are non-destructive such as instrumental neutron activation analysis or methods that involve a complete dissolution of the material prior to performing measurements. For more routine analysis of metals in fertilizer materials, a method was developed and tested by members of the Association of American Plant Food Control Officials (AAPFCO). William Hall initiated the development of this method and Peter Kane coordinated and led this study in which ten laboratories participated. This test method involves microwave digestion with concentrated nitric acid followed by ICP-OES detection and is described in detail elsewhere [1].

Note that this digestion method does not completely dissolve this fertilizer material. Results indicate that some elements are completely extracted but that others are not. The results obtained using this method are shown in Table 1, together with the total element content as determined at NIST for certification of this material, and the percent recovery defined as the ratio of the values obtained from the test method to total element content determined for certification of SRM 695. Collaborating laboratories and analysts are listed in Table 2.

Table 1. Results from Test Method for Determination of As Cd, Co, Cr, Mo, Ni, Pb, and Se in Fertilizers[(a)].

| Element | Test Method Results Average Mass Fraction (1s); Range (mg/kg)[(b)] | % Recovery Average; Range | Total Element Content Mass Fraction (mg/kg)[(b)] |
|---|---|---|---|
| As | 193 (19); 171 – 235 | 96%; 85% - 117% | 200 (5) |
| Cd | 16.1 (2.9); 12.4 - 23.2 | 95%; 74% - 137% | 16.9 (0.2) |
| Co | 47.5 (12.3); 27.4 - 65.7 | 73%; 42% - 101% | 65.3 (2.4) |
| Cr | 174 (19); 136 – 192 | 71%; 56% - 79% | 244 (6) |
| Mo | 14.0 (2.0); 10.2 - 16.8 | 70%; 51% - 84% | 20.0 (0.3) |
| Ni | 112 (15); 85 – 131 | 83%; 63% - 97% | 135 (2) |
| Pb | 257 (15); 231 – 281 | 94%; 85% - 103% | 273 (17) |

(a) Selenium values are not included because the mass fraction of Se in SRM 695 is below the method detection limit.
(b) The values shown here are the certified total element mass fraction values from Table 1 of the Certificate of Analysis.

Table 2. Collaborating Laboratories and Analysts:

| | |
|---|---|
| James Bartos | Division of Regulatory Services, University of Kentucky |
| Rhonda Boles | Experiment Station, University of Missouri |
| M. Dupuis | Ottawa Lab (Carling) Canadian Food Inspection Agency |
| Elaine Hasty | CEM Corporation |
| William Hall, Charles Kinsey and Kwasi Sakyi-Amfo | The Mosaic Company |
| Peter Kane, Sally Mullins and Natalie Newlon | Office of the Indiana State Chemist |
| Judy Purkiss | Michigan Department of Agriculture |
| Christine Rivera | Varian Inc. |
| Wayne Robarge | North Carolina State University |
| Craig Seeley | Teledyne Leeman Labs |
| Sanford Seigel | CF Industries |
| Marcus Svee | Montana Department of Agriculture |
| Terri Van Erem | South Dakota State University |
| Argentina Vindiola | Office of the Texas State Chemist |

REFERENCE

[1] Kane, P.F.; Hall, W.L., Jr.; *Analysis of Arsenic, Cadmium, Cobalt, Chromium, Lead, Molybdenum, Nickel, and Selenium by Microwave Digestion and ICP-OES Detection*: *Collaborative Study*; Paper 2006-17920 of the Office of Indiana State Chemist, Purdue University Agricultural Experiment Station, W. Lafayette, IN (2006).